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Phase transformations in porous Al_2O_3 ceramic nanoclusters

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Abstract : A porous ceramic powder of Al_2O_3 nanoclusters is deduced by a controlled thermal decomposition of a porous $AlO(OH).\alpha H_2O$ powder (porosity Φ = 18%), a precursor of alumina or sapphire, at selected temperatures in the 500-1500 K range. The precursor has been synthesized in a highly pure form using a new chemical method of an electrochemical surface hydrolysis of a thin Al-plate in water. The pores govern a controlled thermal decomposition of it at a molecular scale and result in a refined porous Al_2O_3 powder of an enhanced Φ value up to 40% over the starting value. The sample appears in different polymorphic metastable forms at different temperatures in this range. If compared to in a bulk Al_2O_3, the present transformations occur at significantly reduced temperatures by the assistance of the pores. The results are discussed with microstructure and X-ray powder diffraction studies.

Keywords Al_2O_3 ceramic nanocluster, electrochemical surface hydrolysis, phase transformation

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1. Introduction

Alumina (Al_2O_3) or sapphire forms an important series of ceramic materials with exceptional properties [1-5] such as great hardness, chemical inertness, and a high melting temperature. It has many industrial applications such as in catalysts, coatings, microelectronics, composite materials, and advanced material technology. Besides, the stable phase α-Al_2O_3, it exists in a number of metastable polymorphs, *e.g.*, γ-Al_2O_3, δ-Al_2O_3, θ-Al_2O_3 and ε-Al_2O_3 [6,7]. The structures of the metastable aluminas, also called transition aluminas, can be divided into two main categories based on either a fcc or a hcp arrangement of the atoms. Among them, γ-Al_2O_3 or θ-Al_2O_3 has a fcc structure while ε-Al_2O_3 or α-Al_2O_3 belongs to the hcp structure. In contrast to α-Al_2O_3, there has been much less study on other phases, although they have their own importance in catalysts and other applications.

The recent development in synthesizing of porous Al_2O_3 ceramics and the porous Al_2O_3 reinforced composite materials have generated further new interest in this series [8,9]. They form a host for a uniform intercalation and dispersion of separated particles of pure metals or metal oxides of quantum confined size in the pores and form a variety of optical, magnetic and electronic devices [8-11]. Apart from the electronic applications, they are widely used in adsorption and catalysts where their large surface area, pore structure and surface chemistry play an essential role [9-13]. A porous Al_2O_3 powder is a very useful precursor for synthesis of a porous cermet or other porous ceramic composites.

Several methods using sol-gel and other wet chemical methods are known for synthesis of pure Al_2O_3 ceramics [12-14]. A limitation of all these methods is that they do not give a porous Al_2O_3 powder with a desired porosity. Here, we report synthesis, thermal stabilities, and phase transformations in porous Al_2O_3 clusters. A new chemical method involving an electrochemical surface hydrolysis of a thin Al plate in a pure water [12, 13] and thermal annealing of the obtained product at elevated temperatures are used to synthesize the porous Al_2O_3 powders.

2. Experimental details

The Al_2O_3 nanoclusters in different polymorphic forms are obtained by a thermal decomposition of a porous $AlO(OH).\alpha H_2O$ precursor powder at selected temperatures, in the 500 to 1500K range, in air. The $AlO(OH).\alpha H_2O$ precursor had a porosity ~ 18% and was a pure better than 99.9%. It was obtained by an electrochemical surface hydrolysis of a pure (99.9%) Al-metal plate in a pure water at room temperature [13]. This involves a highly exothermic self-induced spontaneous surface reaction of the Al-metal with the cold water and ultimately yields a nanocrystalline powder (porous) of the

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hydrolyzed Al-metal in $AlO(OH).\alpha H_2O$. The value of $\alpha = 0.76$ is determined by thermogravimetric analysis of its dissociation into Al_2O_3 over 300 to 700 K [13].

The phase analysis was carried by studies of X-ray powder diffractograms for the as received and heated samples at selected temperatures in the 500 to 1500 K range. The diffractograms were recorded with the help a P. W. 1710 X-ray diffractometer using a filtered CoKα radiation of wave length $\lambda = 0.17902$ nm. Their microstructures were studied with a JEOL scanning electron microscope with an *in-situ* analysis of their chemical compositions.

3. Results and discussion

A. Thermal stability and phase transformation :

The as prepared $AlO(OH).\alpha H_2O$ powder has a porosity Φ = 18% as determined by the difference in its theoretical and experimental densities (cf. Table 1). It consists of $AlO(OH).\alpha H_2O$ nanoclusters of a monoclinic crystal system of lattice parameters, $a = 0.866$ nm, $b = 0.506$ nm, $c = 0.983$ nm and $\beta = 94.56°$. Its X-ray powder diffractogram, in Figure 1a, exhibits a total of nine well-resolved peaks in significant intensities over 10 to 100° in the $\theta - 2\theta$ scale. The peaks are characteristically sharp with a no significant scattering background throughout the range. However, some weak unresolved broad bands are superposed over the diffractogram of the resolved sharp peaks. Possibly, these are due to a peculiar porous structure of the sample which has very fine pores of size at a nanometer scale. An average crystallite size D ~ 30 nm is calculated using the Debye-Scherrer analysis [15] of the peak-widths in the sharp diffraction peaks.

The as-received $AlO(OH).\alpha H_2O$ powder is stable as such in ambient atmosphere at room temperatures. On heating over 300 to 1500 K in air, it decomposes into a porous Al_2O_3 powder,

$$2AlO(OH).\alpha H_2O \rightarrow Al_2O_3 + (2\alpha + 1)H_2O. \quad (1)$$

The final Al_2O_3 has a refined microstructure of $AlO(OH).\alpha H_2O$ with a considerably enhanced Φ value. A value of Φ as large as 40% appears in the sample dehydrated at 800 K The crystal structures and densities obtained for the samples dehydrated at selected temperatures are given in Table 1. A refined microstructure in the samples is clearly evidenced by broadened peaks in their X-ray diffractograms.

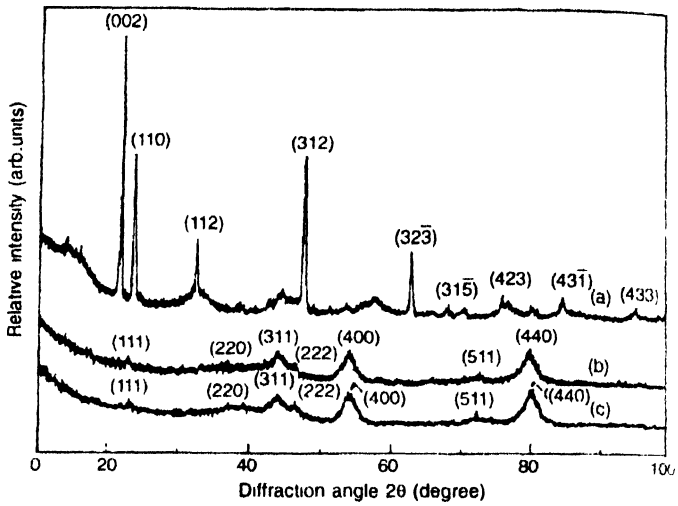

Figure 1. X-ray diffractograms in a controlled thermal decomposition of (a) a porous $AlO(OH).\alpha H_2O$ powder in a porous refined Al_2O_3 powder at (b) 750 K for 2 h and (c) 1050 K for 2h in air

Table 1. Al_2O_3 ceramic powders obtained in different polymorphic forms by a controlled thermal dissociation and reconstructive phase transformation of a porous $AlO(OH).\alpha H_2O$ powder at elevated temperatures

Polymorphic forms	Transformation temperature Porous	Bulk[a]	Crystal structure[a]	Density (g/cm^3) Exp[b]
$AlO(OH)\ \alpha H_2O$	< 310 K		C^1_{2h} Monoclinic	1.90 (2.25)
β- Al_2O_3	Not observed		P6$_3$/mmcHexagonal	(3.24)
γ- Al_2O_3	750 - 1050 K	~ 1070 K	O^7_H-F_{D3M} (fcc, Cubic)	2.20 (3.67)
δ-Al_2O_3	Not observed	~ 1270 K	Orthorhombic	(3.20)
k- Al_2O_3	Not observed	~ 1270 K	Pna2$_1$ Orthorhombic	(3.77)
θ- Al_2O_3	1250 - 1350 K	~ 1370 K	C2/m Monoclinic	2.50 (3.62)
α- Al_2O_3	1400 - 1500K	~ 1650 K	D^6_{3D}-R3c Tetragonal	2.98 (3.99)
ε- Al_2O_3	> 1550 K	> 2200 K	Hexagonal	(4.15)

a) The data are collected from different reports in Refs [1, 3, 5, 13, and 15]

b) The density value calculated from the lattice parameters is included in the parentheses

For example, the X-ray diffractograms obtained for the samples dehydrated at early temperatures as 750 K and 1050 K are compared in Figure 1b and 1c. The both samples have the same peaks with similar peak-widths according to an average crystallite size in the 2 to 5 nm range. All these peaks belong to a single nanocrystalline γ-Al_2O_3 phase. This metastable phase is quite stable in its original cubic crystal structure to a temperature as high as 1100 K. The value of the lattice parameters $a = 0.7860$ nm calculated from the positions of these peaks is in a agreement with the bulk $a = 0.7920$ value [16a].

According to the final temperature and other experimental conditions, the Al_2O_3 so obtained assumes a variety of metastable forms. The different phases are stable over different temperatures. Successive reconstructive phase transformations of a low temperature phase to a high temperature phase occur in the β-Al_2O_3, γ-Al_2O_3, δ-Al_2O_3, k-Al_2O_3, θ-Al_2O_3, α-Al_2O_3 and ε-Al_2O_3 order. In a porous precursor used in this example, these transformation occurs at moderate temperatures if compared to those in a bulk precursor derived from a sol-gel chemistry or other wet methods [14]. For example, the α-Al_2O_3 phase appears with Φ = 25% at as early temperature as 1450 K against 1650 K in the bulk AlO(OH).αH_2O (or γ-Al_2O_3) precursor. The pores govern a controlled microstructure of the final phase in a quantum confined size at a nanometer scale. This is not possible with a sol-gel and other wet methods in which the AlO(OH).αH_2O precursor molecules are strongly correlated one another through a strong hydrogen bonding. Under identical conditions, these do not disperse in a refined microstructure with a significant Φ value.

The formation and thermal stabilities of the different Al_2O_3 polymorphs are determined by studies of the X-ray diffractograms of those obtained at different temperatures. For example, the diffractograms obtained for the θ-Al_2O_3 and α-Al_2O_3 polymorphs at 1250 K and 1450 K are shown in Figures 2 and 3. A complete list of the different phases observed in this investigation is summarized in Table 1. The most stable phase in this series at a temperature as high as 1500 K is the α-Al_2O_3 phase. It has a D^6_{3D}-R3c tetragonal crystal structure of lattice parameters of a = 0.4102 nm and c = 1.3020 nm. These lattice parameter values are modified a little in comparison with the standard values [16b], a = 0.4758 nm and c = 1.2991 nm, so that they involve ~ 25% lower lattice volume. It appears that the pores support the formation of a more distortion free lattice according to its lower volume (or the Gibb's free energy).

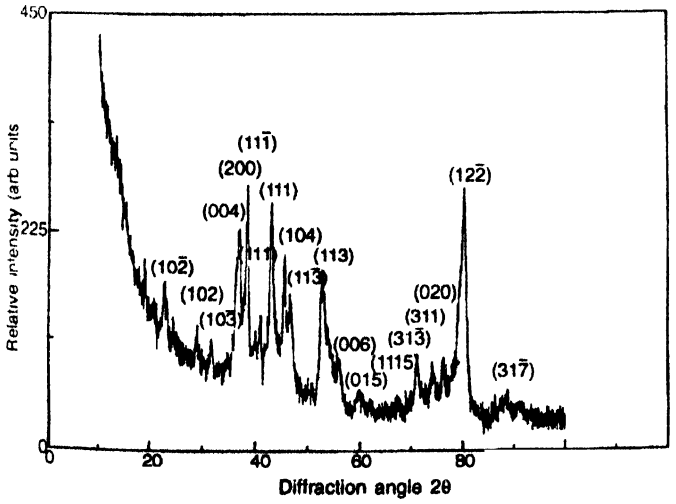

Figure 2. X-ray diffractogram for a porous refined θ-Al_2O_3 powder obtained by a controlled thermal decomposition of the porous AlO(OH).αH_2O powder at 1250 K for 2 h in air.

B. Microstructure :

We analyzed microstructures of the representative samples with their scanning electron micrographs (SEM). Several micrographs were recorded at different magnifications in an attempt to resolve the size and morphology of the particles and/or crystallites. A

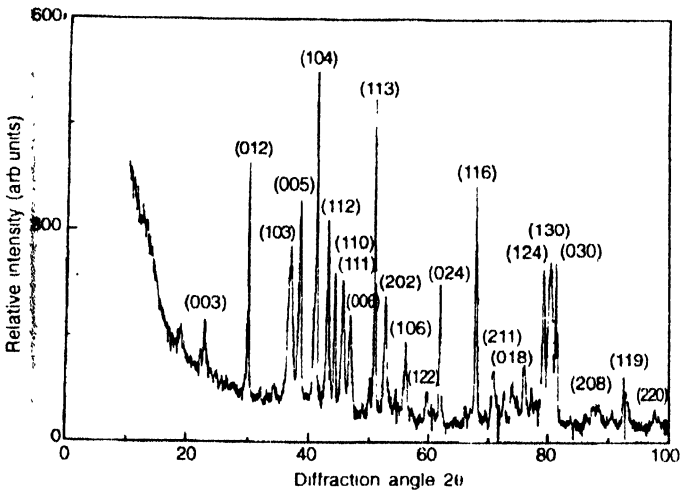

Figure 3. X-ray diffractogram for a porous refined α-Al_2O_3 powder obtained by a controlled thermal decomposition of the porous AlO(OH) αH_2O powder at 1450 K for 2 h in air

typical set of the SEM micrographs for the sample of γ-Al_2O_3, processed at 750 K for 2h, is shown in Figure 4. The micrographs *a*, *b* and *c* in this figure are recorded at three different magnifications. None of them presents a resolved structure of the particles and/crystallites with a defined size or morphology of them. Perhaps, this is due to a peculiar porous structure of the sample in which the pores and the particles/crystallites are intimately correlated one another at a nanometer scale with a strong macroscopic interaction. As mentioned above, an average crystallite size of 2 to 5 nm is obtained by the peak-widths in the characteristic X-ray diffraction peaks. It seems to be very much consistent with a similar small value in these micrograms. Therefore, it is not resolved in these particular micrographs.

According to the microstructure, the structure as well as the average size of the particles does not change much on raising the processing temperature. For example, a set of three other micrographs for a sample (α-Al_2O_3) processed at a temperature as high as 1450 K is shown in Figure 5. The structure is a more or less the same as shown above (in Figure 4) for the sample processed at 750 K. An important implications of these results is that the fine pores in the precursor play a vital role in deterring the process of the phase transformation and evolution of the final microstructure. A similar Al_2O_3 sample derived from a sol-gel or other wet methods under identical conditions presents a much coarser microstructure at a micrometer scale [14,17].

4. Conclusions

The work in this article, demonstrates phase transformation in porous aluminas. It is observed that a controlled thermal

decomposition of a nanostructured porous AlO(OH).αH_2O precursor in air designs in a porous Al_2O_3 ceramic powder of a refined microstructure. Successive reconstructive phase transformations in the various well-known Al_2O_3 polymorphs (except the ε-Al_2O_3 one that occurs above 1500 K) appear at different temperatures in the 500-1500 K range. Unusually, the apparent microstructure of the specimen of refined pores and particles /crystallites does not change much with a variation of the processing temperature in the different polymorphs. The result is very useful in designing of a porous Al_2O_3 and its

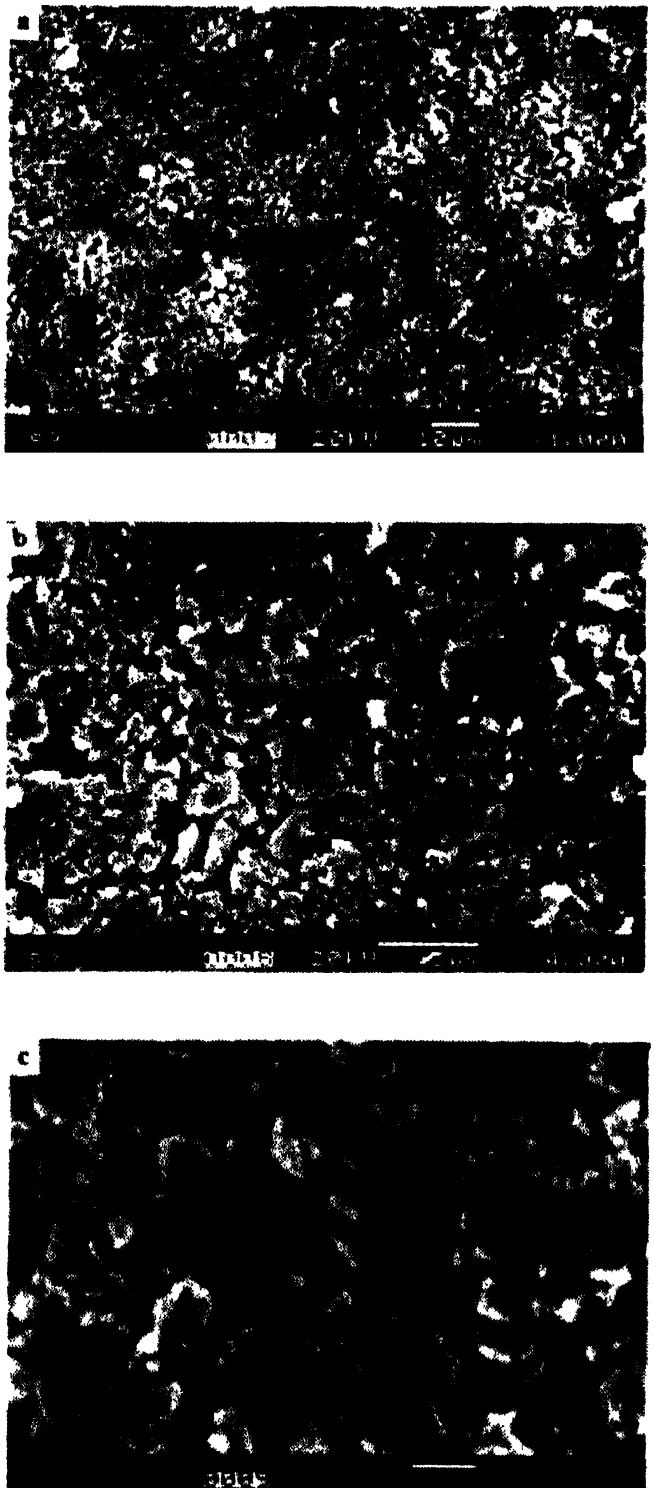

Figure 4. SEM micrographs of a porous refined γ-Al_2O_3 powder obtained by a controlled thermal decomposition of the porous AlO(OH).αH_2O powder at 750 K for 2 h in air. The three (a), (b), and (c) micrographs are obtained at three different magnification as marked over them.

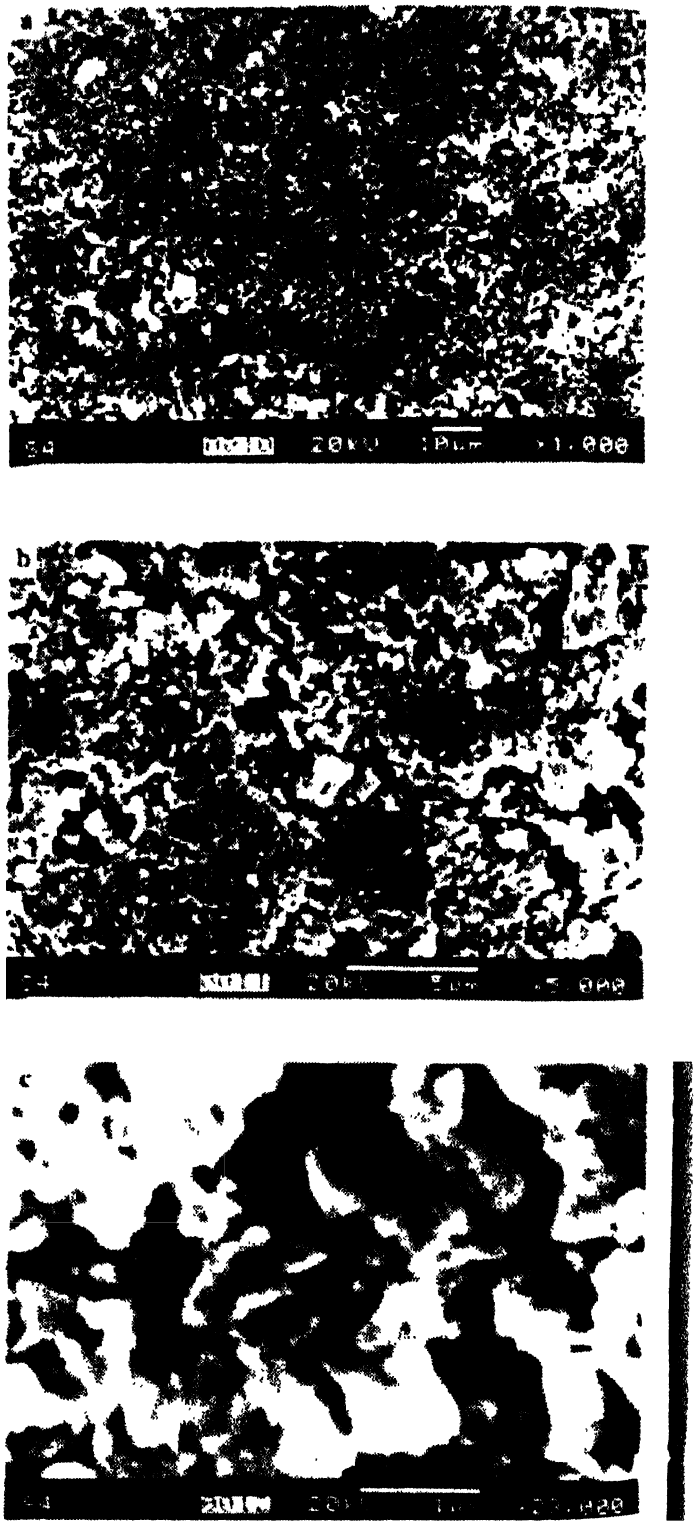

Figure 5. SEM micrographs of a porous refined α-Al_2O_3 powder obtained by a controlled thermal decomposition of the porous AlO(OH) αH_2O powder at 1450 K for 2 h in air. The three (a), (b), and (c) micrographs are obtained at three different magnification as marked over them

composites in a controlled quantum confined particle size at a nanometer scale.

Acknowledgments

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